

Characterization and Flux of Marine Oil Snow in the Viosca Knoll (*Lophelia* Reef) Area due to the Deepwater Horizon Oil Spill

Scott A. Stout¹ and Christopher R. German²

¹NewFields Environmental Forensics Practice, LLC, Rockland, MA

²Woods Hole Oceanographic Institution, Woods Hole, MA

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Summary

Sediment trap samples from the Viosca Knoll (*Lophelia* reef) shelf edge area (VK826), approximately 60 km northeast of the failed Macondo well, were collected before, during and after the *Deepwater Horizon* oil spill. Detailed chemical analyses were performed on the <1 mm particulate fraction in order to assess the presence, character and sedimentation rate of any Macondo oil impacting the reef ecosystems in this area. This study contributes to the understanding of the so-called “*marine oil snow sedimentation and flocculent accumulation*”, or MOSSFA, caused by the *Deepwater Horizon* oil spill. The following conclusions are reached:

- The sedimentation rates of conventional metrics, viz., total mass of particulate (< 1 mm) and particulate organic carbon (POC), provide no basis upon which to recognize an impact of the *Deepwater Horizon* oil spill in the Viosca Knoll area.
- On the other hand, sedimentation rates of hydrocarbons – measured as total petroleum hydrocarbons (TPH), total polycyclic aromatic hydrocarbons (TPAH50), and hopane – in the trap particulates show dramatic increases, more than an order of magnitude above pre- and post-spill background values, coincident with the active *Deepwater Horizon* oil spill (April 20 to July 15, 2010).
- During the active spill period, the seven trap samples from the VK826 site had average sedimentation rates for TPH, TPAH50, and hopane of 2,356, 5.4 and 0.89 $\mu\text{g}/\text{m}^2/\text{day}$, respectively, which are markedly (19 to 44 times) higher than had existed prior to the spill. On average, after the active spill hydrocarbon fluxes largely return to pre-spill conditions.
- The timing of its appearance and its chemical fingerprint (e.g., biomarkers) clearly establishes that the oil detected in the trap samples during April-July 2010 was Macondo oil released during the *Deepwater Horizon* oil spill.
- All of the settling Macondo oil collected in this area had been partially evaporated and exhibited evidence of photo-oxidation, indicating it had originated from oil that had been at the sea surface (*versus* the deep-sea plume, which could not have reached up to the shallow depths of Viosca Knoll on the northern GoM shelf at ~400-450 m). Over the duration of the active spill the oil settling in this area became increasingly biodegraded.
- Two distinct maxima, or “pulses” of oil deposition, were recognized during the active spill that are likely attributed to a combination of factors that included the persistence of floating oil in the area (oil days), surface application of dispersants, algal/bacterial populations, abundance of mineral matter, and the hydrodynamic conditions affecting the collision rates among oil and any (organic or inorganic) particles.
- Based on the measured sedimentation rates for hopane, a presumed conservative marker, it is estimated that ~10 barrels (bbl) per km^2 of Macondo oil was deposited in the VK826 area during the active spill. By extension, it is estimated that more than



76,000 bbl of oil once present at/near the surface sank over the approximately 7600 km² area that, based upon a comparable or higher number (>30) of surface oil days as experienced by the VK826 site, was most intensely impacted by sinking surface oil.

- This 7600 km² area encompasses, but is 5- to 7-times larger than, the previously-recognized deep-sea, surface sediment (< 1cm) “footprint” (1030 to 1910 km²; Stout et al., 2015), which was based on sediment chemistry of more than 700 sediment cores. Notably, about half this 7600 km² area covers relatively shallow (<1000 m) regions (including the Viosca Knoll *Lophelia* reefs) where the seafloor was not previously recognized to have been impacted by Macondo oil.
- The estimated volume of previously-unrecognized sunken surface oil (65,700 to 56,900 bbl) demonstrated through this study increases the total volume of Macondo oil previously-recognized within the deep-sea, surface sediment “footprint” (152,000 to 173,000 bbl; Stout et al., 2015) by 33 to 43 vol%.
- The same results also allow us to estimate that the MOSSFA flux identified here would only have contributed approximately 10% (7-11%) of the total input to the seafloor within the area of the deep-sea, surface sediment “footprint” that was previously recognized. Within that more restricted area, the vast majority of the oil deposited (89-93%) was derived, as reported elsewhere, from the deep-sea plume.
- In total, sediment core-based oil volumes in the deep-sea (>1000 m; Stout et al. 2015) and sediment trap-based oil volumes in shallower regions (< 1000 m) indicate at least 217,700 to 229,900 bbl of oil ended up on at least 7600 km² of the seafloor surface following the *Deepwater Horizon* oil spill (Table 4).

Introduction

The *Deepwater Horizon* oil spill introduced approximately 4 millions of barrels of oil to the northern Gulf of Mexico at a depth of approximately 1500 meters (Crone and Tolstoy, 2010). Some fraction of the Macondo crude oil released remained in the deep-sea as a dissolved phase and as physically or chemically-dispersed, neutrally buoyant droplets, both of which were transported laterally at depths of ~1000 to 1300 meters (Camilli, et al. 2010; Socolofsky et al. 2011), i.e., the deep-sea plume. Some fraction of the dispersed oil within the deep-sea plume ultimately was deposited on the seafloor (and deep-sea corals) associated with a brown flocculent material, or floc (White et al., 2012; Stout, 2015a). In addition, a buoyant fraction of the oil released traveled to the sea surface where it was spread by wind and currents over vast areas of the northern Gulf of Mexico for nearly 3 months following the explosion before dissipating about 5 weeks after the well was capped on July 15 (Ramseur, 2010). The oil that had reached the surface was subject to weathering (e.g., Aeppli et al., 2012), *in situ* burning (Mabile and Allen, 2010), and dispersant application, which, facilitated by an association with prolific biomass growth, caused some of the surface oil to lose its buoyancy and sink back through the water column (Passow et al. 2012; Passow, 2014). The phenomenon and pathways by which Macondo oil from the deep sea plume or from the surface ended up on the seafloor has been collectively referred to as “*marine oil snow sedimentation and flocculent accumulation*” or MOSSFA (Kinner et al. 2014).

Chemical evidence for the MOSSFA is indicated by the elevated concentrations of hydrocarbons in surface sediments (e.g., hopane; Valentine et al. 2014) and by chemical fingerprinting of sediment cores (Stout 2015a; Stout et al. 2015). These sediment-based studies show that the impacted areas are largely restricted to sediments >1000 m deep, i.e. within the deep-sea. The occurrence of impacted sediments at depths >1000 m and in a pattern that is skewed toward the southwest along the prevailing deep-sea current's



direction suggests the seafloor impact is reasonably attributable to the deposition of oil derived predominantly from the deep sea plume (Valentine et al., 2014), which had only existed at depths >1000 m (Camilli et al., 2010). Not surprisingly, exposure of benthic ecosystems >1000 m to Macondo oil has been confirmed by visible, biological, and/or chemical evidence at numerous deep water coral communities (White et al., 2012; Hsing et al. 2013; Fisher, et al. 2014; e.g., MC294, MC297, and to a lesser extent MC344) and in soft-bottom benthic infauna (Montagna et al. 2013).

Evidence for the MOSSFA and exposure to Macondo oil of shallower (<1000 m) ecosystems, i.e., those shallower than the top of the deep sea plume has, until now, been lacking. For example, examination of two colonial coral sites north of the Macondo wellhead (VK906 and VK826; Fig. 1) did not exhibit visible signs of impact (Fisher et al. 2014) and sediment cores collected at <1000 m depth, though only sparsely represented by a limited number of cores (Fig. 1), indicated no obvious evidence for impact by Macondo oil (Montagna et al. 2013; Valentine et al. 2014; Stout 2015a). Therefore, to date, there has been a general lack of evidence for the MOSSFA and exposure in these shallower ecosystems.

In this study, we present the results of chemical analysis of marine oil snow captured in sediment traps in the Viosca Knoll area (VK906 and VK826, the latter in particular) that challenge that paradigm (Fig. 1). The traps were located approximately 37 and 58 km from the Macondo well in water depths of approximately 400-450 m and proximal to *Lophelia* reef ecosystems that were already known to exist in both areas. The VK826 samples collected span the time from September 2009 to September 2011, i.e., before, during, and after the *Deepwater Horizon* oil spill. The results provide an unequivocal basis upon which to recognize the presence, weathering characteristics, sedimentation rate and duration of the Macondo-derived marine oil snow deposited in the Viosca Knoll area during the spill. The results will demonstrate that (1) Macondo oil from the sea surface (and not only from the deep-sea plume) sunk to the seafloor and (2) this phenomenon impacted shallower (<1000 m) benthic ecosystems, at least in the Viosca Knoll area, but likely was much more widespread.

Sediment Traps and Samples

Figure 1 shows the locations of the Viosca Knoll sediment traps and additional details are given in Table 1. All of the (McLane Mark-7 type) sediment traps had a 0.5 m² collection area and had 13 or 21 collection cups. A complete inventory of 71 individual samples from these traps is given in Attachment 1.

Prior to the start of the *Deepwater Horizon* oil spill on April 20, 2010, a sediment trap was deployed in the VK826 area as part of on-going NOAA and Minerals Management Service (now Bureau of Ocean Energy Management) *Lophelia* II research program concerning the well-studied *Lophelia pertusa* deep, cold-water reef ecosystem that exists in the area (e.g., Sulak et al. 2008). After the spill began, additional sediment traps were deployed in the VK826 and VK906 areas through funding provided by the National Science Foundation's Rapid Response Research grant and from NOAA's NRDA (Table 1). In addition, a limited number of samples collected before the start of the spill were available from a sediment trap located in the Mississippi Canyon (MC751) area approximately 153 km southwest of the Macondo well.

Of greatest relevance to this study, the three different traps deployed in the VK826 area provide an uninterrupted sample set (n=47) that, with a 14- or 15-day temporal resolution, spans 733 days. These 733 days include 221 days before the *Deepwater Horizon* oil spill commenced, the 87 days of the active spill (April 20, 2010-July 15,



2010), and 426 days after the well was shut-in (Table 1). The two different traps deployed in the VK906 area provide a sample set (n=20) spanning 90 days beginning two weeks after the Macondo well was capped and overlapping, temporally, with a subset of the samples collected at the adjacent VK826 site (Table 1).

The sediment trap samples were preserved *in situ* during collection with 20% buffered dimethyl sulfoxide (DMSO) and upon retrieval were stored cold (5°C) and dark until processing at the Woods Hole Oceanographic Institution (WHOI) laboratory. Each sample was wet sieved through 5-mm (intended to remove “swimmers”) and then 1-mm sieves.

All sample fractions were visually inspected as there was *a priori* expectation that some oil could be present. However, there was no visual evidence for oily snow particles and/or adhered oil in the < 1 mm, 1-5 mm, or > 5 mm fractions; i.e., by visual accounts the samples appeared typical of sediment trap samples unrelated to any oil spill. On average, the < 1 mm fraction represented >95% of the total mass and therefore, our analytical efforts were focused on this fraction, as is standard practice for ocean biogeochemistry sediment trap investigations (Honjo et al. 2014).

Aliquots of the <1 mm size fraction were wet-split into 10 parts (RSD of 5%) with four being used for multiple analyses, including particulate organic carbon (POC) and sample dry weight. The remaining six aliquots of each sample were individually prepared for hydrocarbon analysis by rinsing with distilled water over a 0.3 µm pore 47 mm glass fiber filter (GFF) in order to remove any (operationally-defined) dissolved hydrocarbons. The six aliquots for each sample were then stored wet in a 10% buffered DMSO solution sealed in six 50 mL polypropylene centrifuge tubes and refrigerated (5°C).

The individual sample masses for the 71 samples (< 1 mm) available for the chemical analysis described herein ranged from 26 mg to 9.8 g dry weight, of which approximately 80% was used for the analyses described below.

Methods

The six aliquots for all 71 sediment trap samples (< 1 mm) for chemical analysis were transferred from WHOI to Alpha Analytical Laboratory (Mansfield, MA) under full chain-of-custody on September 12, 2013. Samples were stored cold (4°C) and dark until sample preparation.

Five of the six aliquots from each sample were centrifuged at 3500 RPM for 5 minutes and the supernatant was decanted and archived. (One aliquot for each sample was archived and later returned to WHOI.) Particulates from each of the five aliquots representing a single trap sample were rinsed from each vial with deionized water and composited upon transfer to an extraction jar. The extraction jar was then centrifuged at 3000 RPM for 5 minutes and the supernatant was filtered through pre-cleaned (baked 400°C for 1 hour, rinsed in dichloromethane and air-dried) 0.4 µm pore 47 mm GFF. The filter was then transferred back into the extraction jar to be extracted along with the particulate. The filtrate was archived.

The composited particulate/filter from each sediment trap sample was then spiked with recovery surrogates and serially-extracted (3x) using fresh dichloromethane (DCM). Each sample's serial extracts were combined, dried with sodium sulfate, and concentrated. The concentrated extracts were then processed through silica gel, eluting with DCM, following adaptations of EPA Method 3630. The silica-cleaned extracts were then concentrated and spiked with internal standards prior to instrument analysis. The extracts were analyzed in accordance with NOAA (2014) via:



- (1) *Total Petroleum Hydrocarbons (TPH) and Saturated Hydrocarbon (SHC) Quantification and Fingerprinting:* a modified EPA Method 8015B was used to determine the TPH concentration (C_9 - C_{44}) and concentrations of individual *n*-alkanes (C_9 - C_{40}) and (C_{15} - C_{20}) acyclic isoprenoids via gas chromatography-flame ionization detection (GC/FID). The percent dry weights determined by WHOI were used so that TPH and SHC concentrations were reported in $\mu\text{g/g}$ dry weight.
- (2) *PAH, Alkylated PAH and Petroleum Biomarkers:* a modified EPA Method 8270 was used to determine the concentration of (1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids via GC/MS operated in the selected ion monitoring mode (SIM). The percent dry weights determined by WHOI were used so that target analyte concentrations were reported in $\mu\text{g/g}$ dry weight.

The target analytes for this analysis are listed in Attachment 2. Note that two PAH totals are given, viz. TPAH16 and TPAH50. TPAH16 represents the total of 16 Priority Pollutant PAH analytes (see bold; Attachment 2) and TPAH50 represents the total concentration of all 2- to 6-ring PAH analytes ranging from naphthalene to benzo(*g,h,i*)perylene, excluding perylene.

The TPH, SHC, PAH and biomarker concentration data reported herein are non-surrogate corrected. The analytical results for all 71 samples were also reported through NOAA DIVER as surrogate corrected results. Several samples had TPH concentrations reported below the sample specific reporting limit (i.e., reported concentrations were J-qualified and considered estimates; Attachment 1); these were converted to non-detected in DIVER, but were utilized as reported herein.

The relative (hopane-normalized) concentrations of PAH and biomarkers in the sediment trap samples studied are compared to those of fresh Macondo reference oil (Stout, 2015b) and floating Macondo oils ($n=62$) collected during the active spill (Stout, 2015c). In addition, limited data (publically-available, obtained from NOAA's DIVER database) for six sediment cores collected in the VK826 and VK906 areas in October 2011 (Holiday Chouest 3 cruise, Oct. 1-25, 2011) are presented.

Hydrocarbon sedimentation rates (flux) for TPH, TPAH16, TPAH50, and hopane ($\mu\text{g}/\text{m}^2/\text{day}$) were calculated by multiplying the concentration of these hydrocarbons in trap samples ($\mu\text{g}/\text{g}_{\text{dry}}$) by the total mass of particles ($< 1 \text{ mm}$) in the trap samples (g_{dry}) divided by 0.5 m^2 (surface area of the trap) then divided by the number of days during which each sequential sample cup was rotated into the open collection position (days):

$$\text{Flux } (\mu\text{g}/\text{m}^2/\text{day}) = [(\text{Conc } \mu\text{g}/\text{g}_{\text{dry}}) \times (\text{Mass } \text{g}_{\text{dry}})] \div 0.5 (\text{m}^2) \div \text{days} \quad \text{Eq. (1)}$$

Hopane ($17\alpha(\text{H}), 21\beta(\text{H})$ -hopane) was one of the targeted petroleum biomarkers, which is recognized to be highly recalcitrant to oil weathering processes (Prince et al. 1994). After correcting for any pre-spill deposition of hopane, the sedimentation rate of hopane in those trap samples recognized to contain Macondo oil was used to estimate the sedimentation rates of Macondo oil on a mass basis ($\text{kg}/\text{km}^2/\text{day}$) and volume basis



(barrels/km²/day), using the previously-determined concentration of hopane (68.8 µg/g; Stout, 2015b) and density (0.856 g/ml at 5°C; Stout, 2015d) of fresh Macondo oil (see below). The sedimentation rates, mass, and volumes of Macondo oil calculated are considered conservative as they assume hopane was not weathered.

Results and Discussion

Tabulated concentration data and corresponding sedimentation rates for the 71 sediment trap samples discussed herein are found in Attachment 1.

Conventional Flux Metrics

Figure 2 shows the temporal trend in the sedimentation rates of total particulate mass (<1 mm) and particulate organic carbon (POC) for the sediment trap samples studied. The shaded area spans the time interval of the *Deepwater Horizon* oil spill (April 20-July 15, 2010). Inspection reveals that there is a good correlation between the total particulate mass and POC sedimentation rates for the Viosca Knoll trap samples (but less so for the few Mississippi Canyon trap samples), however there is no obvious relationship between either of these and the oil spill. The VK826 location shows a minor increase in both sedimentation rates in the last few weeks of the active oil spill, which could be associated with settling of biomass and/or oil associated with the oil spill. However, comparable increases were also observed at this location long before and after the spill. The VK906 location exhibits sporadic increases and decreases in the sedimentation rates of both the total mass and POC, but these occur in August through early October, i.e., 1 to 3 months after the spill had ceased. Therefore, collectively the sedimentation rates of the total mass of particulate (< 1 mm) and POC provide no clear basis upon which to recognize the MOSSFA associated with the *Deepwater Horizon* oil spill in the Viosca Knoll area.

Hydrocarbon Concentrations

Figure 3 shows the temporal trends in the concentrations of TPH, TPAH50, and hopane in the trap particulate samples over the study period. As can be seen the largely uninterrupted sample set for the VK826 site provides a complete record spanning from up to 221 days before to 512 days after the *Deepwater Horizon* disaster on April 20, 2010. A smaller sample set exists for the nearby VK906 site for 14 to 104 days after the Macondo well was shut-in and the leak stopped on July 15, 2010.

At the VK826 location all three hydrocarbon trends show dramatic increases, approaching two orders of magnitude, in the concentrations of TPH, TPAH50, and hopane in trap particulates coincident with the *Deepwater Horizon* oil spill (Fig. 3). Specifically, hydrocarbon concentrations increased sharply between the samples collected April 9 to 23, 2010 and April 23 to May 7, 2010, which coincides with the *Deepwater Horizon* explosion on April 20 and subsequent sinking of the rig on April 22, 2010. Elevated concentrations of hydrocarbons persisted throughout the 90-day spill but showed two distinct maxima, or “pulses”, separated by an interval of lower concentrations (Fig. 3). Possible causes for these “pulses” are discussed further below. Finally, there was a rapid decrease in hydrocarbon concentrations in the particulates at VK826 quickly after the spill ended July 15, 2010. Low concentrations then persisted throughout the post-spill sampling interval (Fig. 3).



Hydrocarbon Flux

Although revealing, the hydrocarbon concentrations in trap samples (Fig. 3) reflect variations in the amounts of *both* oil and any non-oil (e.g., biomass or mineral matter) components present in the sediment trap samples, and therefore it is more appropriate to examine any temporal trends using hydrocarbon sedimentation rate, or flux. (All individual samples' calculated sedimentation rates are found in Attachment 1.)

The fluxes calculated for TPH, TPAH50, and hopane for the sediment trap samples from the VK826 site are plotted in Figure 4. Table 2 provides the average sedimentation rates for the VK826 trap samples representing the pre-spill, spill, and two post-spill periods. Hydrocarbon flux rates calculated for the VK906 and MC751 trap samples (Attachment 1) are not discussed due to their limited durations which we know, from comparison with the VK826 data, fall outside the window of spill-impacted sediment-trap flux. As noted above, however, hydrocarbon concentrations at both of these additional sites, at the times for when data ARE available, generally matched those present at VK826 prior to (MC751) and after (VK906) the spill (Fig. 3).

Markedly higher sedimentation rates of TPH, TPAH50, and hopane existed at the VK826 site during the active *Deepwater Horizon* oil spill (Fig. 4). The seven trap samples collected during the active spill (points B through H; Fig. 4) had average sedimentation rates for TPH, TPAH50, and hopane of $2,356 \pm 1,919$, 5.4 ± 5.7 and 0.89 ± 1.0 $\mu\text{g}/\text{m}^2/\text{day}$, respectively (Table 2). These average sedimentation rates during the spill are markedly (19 to 44 times) higher than existed prior to the spill (Table 2), which clearly reveals that the deposition of oil in the VK826 area was coincident with the active *Deepwater Horizon* oil spill. By extension, it is reasonable to believe that sedimentation of oil was occurring beneath a much larger area than represented by the VK826 sediment trap. Additional discussion of this is given later in this report.

During the active spill there were two distinct "pulses" of hydrocarbon sedimentation (Fig. 4), which were also apparent in the hydrocarbon concentration data (Fig. 3). The first "pulse" of oil occurred during the first four weeks of the spill (April 23-May 21; sample points B and C; Fig. 4), before declining slightly over the next four weeks (May 21-June 18; sample points D and E; Fig. 4). The second "pulse" of oil was then observed (June 18-July 25; sample points F to H; Fig. 4). The second "pulse" exhibited markedly higher oil sedimentation rates than the first "pulse" had, the latter exhibiting maxima of 5,756, 17.5, and 2.9 $\mu\text{g}/\text{m}^2/\text{day}$ of TPH, TPAH50, and hopane, respectively (sample points G, Fig. 4).

Further discussion as to the cause(s) for the two "pulses" of oil arriving at the VK826 trap is warranted. Comparison of Figures 2 and 4 reveal that the first "pulse" of oil (sample points B and C) was accompanied by only slight increases in both the total mass of particles and POC whereas the second "pulse" of oil (sample points F and G) was accompanied by larger increases in both (Fig. 2). This relationship between the fluxes of oil and total mass and oil and POC can be more easily seen in Figure 5, which shows the flux of hopane versus those for total particulate mass (Fig. 5A) and POC (Fig. 5B) for the VK826 sediment trap samples before, during and after the active spill. The markedly higher fluxes of oil (represented by hopane), total particulate mass, and POC are clearly evident during the active spill, being highest during the second "pulse" of oil (sample points F to H; June 18-July 25).

Thus, there is a clear relationship between the amounts of total particulate mass or POC sinking through the water column and the amount of oil being transported to the seafloor. We attribute this relationship to the formation of mucous-rich marine snow that was



observed to form *in situ* at the sea surface during the active spill (Passow et al., 2012). Specifically, phytoplankton under stress produce a mucous-like, sticky (extracellular polymeric) substance that promotes their aggregation and sinking, a process which is hypothesized to have carried the spill oil from the surface to the seafloor (Passow, 2014) or to have scavenged chemically dispersed oil from the water column (Fu et al., 2014).

This “marine oil snow” hypothesis is clearly supported by the VK826 sediment trap results, which demonstrate that two distinct marine oil “snow storms” occurred in the VK826 area resulting in two “pulses” of oil being transported to the seafloor (Fig. 4). A combination of factors were likely involved in the promoting these two marine oil snow “storm” events in the VK826 area during the active spill. These factors likely included temporal variations in (1) the persistence of floating oil in the area (e.g., oil days), (2) the surface application of chemical dispersants in the area, (3) plankton and bacterial populations, (4) abundance of mineral matter, and (5) the hydrodynamic conditions affecting the collision rates among oil and any (organic or inorganic) particles in the water. Based upon the sediment trap results, the combination of factors were most favorable for the formation and sedimentation of marine oil snow in the VK826 area during the second “pulse” of oil that occurred later in the spill between June 18-July 25 (sample points F to H; Figs. 4 and 5).

Notably, only shortly after this second “pulse” of oil the sedimentation rates quickly dropped to rates mostly consistent with those that existed prior to the spill (Fig. 4; Table 2). The average post-spill flux for hopane is only marginally higher than what had existed prior to the spill (Fig. 4), and given the error among these average rates (Table 2) provides equivocal evidence for the persistence of any “lingering” oil following the end of the active spill. The fingerprinting results presented below, however, further address this possibility.

The obvious temporal relationship between hydrocarbon fluxes in the Viosca Knoll 826 area and the duration of *Deepwater Horizon* oil spill (Fig. 4; Table 2) provides strong evidence that Macondo oil (and not some “other” oil) was settling through the water column at this time. Additional evidence for the presence of Macondo oil and its degree of weathering is provided in the detailed characteristics of these hydrocarbons, as discussed in the following sections.

Total Petroleum Hydrocarbons

Figure 6 shows a series of GC/FID chromatograms that reveal the nature of the TPH found in trap samples collected before, during, and after the *Deepwater Horizon* oil spill. Prior to the spill the sediment trap samples’ TPH chromatograms were dominated by discrete, resolved peaks and no unresolved complex mixture (Fig. 6A). GC/MS revealed some of the smaller resolved peaks were odd-carbon n-alkanes typical of epicuticular higher plant waxes (Fig. 6A; Eglinton and Hamilton 1967). The larger peaks, however, were tentatively identified as branched alkenes and cyclic terpenoids (see triangles; Fig. 6) likely associated with recent marine biomass – not petroleum.

The GC/FID chromatograms for the TPH in the seven samples collected during the spill exhibit clear evidence for the presence of crude oil, however the extent of weathering of the oil progressively varies over time (Fig. 6B-H). The earliest sample collected during the spill contains crude oil that exhibits a relatively small unresolved complex mixture (UCM) atop of which are a series of n-alkanes ranging from n-C₁₅ to n-C₄₀, reaching a maximum around n-C₂₀ (Fig. 6B). Pristane and phytane are present, though in lower concentrations than the corresponding n-alkanes. The features of this “first arriving” oil



are consistent with Macondo oil that has experienced evaporative losses of most compounds below n-C₁₅ while evidence for biodegradation is not (yet) evident.

Over time however, the crude oil present in the trap samples exhibits signs of increased weathering, particularly biodegradation (Fig. 6C-H). There is a progressive loss in n-alkanes, which are the hydrocarbons in crude oil that have long been recognized to be those most highly susceptible to biodegradation (Peters and Moldowan, 1993). Eventually, only the longer chain n-alkanes (n-C₂₈ to n-C₄₅, reaching a maximum around n-C₃₃) are retained (Fig. 6H). The more resistant acyclic isoprenoids, pristane and phytane, are initially preserved (Fig. 6B-F), but they too are depleted or absent due to biodegradation in the later trap samples (Fig. 6G-H). Over time the shape of the UCM progressively shifts toward higher and higher boiling range material, reflecting an overall greater loss of smaller, lower boiling hydrocarbons. The steady progression in weathering represented by the first four samples collected during the spill (Fig. 6B-E) is interrupted by the somewhat “fresher” character of the oil present in the fifth sample collected (Fig. 6F). Notably, the arrival of this slightly less weathered oil coincides with the onset of the second “pulse” of oil that arrived at the VK826 trap later in the oil spill (Fig. 4).

There is a notable variation in the relative abundance of the biomass-related compounds versus oil among the chromatograms containing oil (see triangles; Fig. 6B-H) that also follows the “two pulse” trend. Specifically, the samples represented by the first “pulse” of oil (Fig. 6B-D) contain a greater relative (to oil) abundance of biomass-related compounds than the samples represented by the second “pulse” of oil (Fig. 6E-H). Although the higher concentrations of oil in the latter may play a role, it is also possible that the abundance of these particular biomass-related compounds may reflect different types of biomass within the samples. Specifically, the particular biomass that participated in the first “pulse” of marine oil snow may have been different from the biomass that participated in the second “pulse”. Because the oil in the first “pulse” was less biodegraded than the oil in the second “pulse” one might speculate that the dominant biomass promulgating these two marine oil snow events were (non-oil-degrading) phytoplankton and oil-degrading bacteria, respectively.

As noted above, on average, the flux of TPH after the active spill returned to levels comparable to those that existed prior to the spill (Table 2). Thus, although TPH flux rate alone cannot argue that there is any lingering oil being transported to the seafloor after the spill, the character of the TPH arriving at the trap after the spill exhibits some evidence in support of this possibility. For example, Figure 6I shows that the sediment trap TPH exhibits a trace UCM and minor longer chain n-alkanes (with no odd-carbon dominance) that were not present prior to the spill, features that suggest some traces of lingering oil may still be present in the weeks following the end of the active spill.

It is notable that there is clear evidence for biodegradation of the oil arriving at the trap throughout the duration of the spill (Fig. 6; see above). Virtually no biodegradation was observed among the population of 62 Macondo surface slicks, mounds, and sheens collected at the sea surface between May 10 and June 20, 2010 (Stout, 2015c). The lack of biodegradation among these floating oils was attributed to the inability for biodegradation to advance quickly within the concentrated surface oils. The sediment trap results, however, indicate that biodegradation was able to affect the oil that sank through the water column, likely facilitated by chemical dispersants. This suggests that, as intended, dispersants applied to surface oil allowed biodegradation to proceed within



dispersed oil droplets. Because the “first arriving” oil reaching the trap was not biodegraded (Fig. 6B) it seems possible that there may have been an initial lag in the ability of indigenous bacteria to respond to the oil’s presence within the water column. Throughout the course of the 87-day spill, however, biodegradation of the settling oil within the water column appears to have progressed aggressively (Fig. 6B-H).

PAHs

Figure 7 shows hopane-normalized histograms showing the relative abundance and distributions of PAHs in the trap samples collected before, during, and after the *Deepwater Horizon* oil spill. Prior to the spill only low fluxes of TPAH were evident in the VK826 trap samples (Fig. 4B) averaging $0.20 \pm 0.16 \mu\text{g}/\text{m}^2/\text{day}$ TPAH50 (Table 2). These were comprised predominantly of numerous Priority Pollutant PAHs (Fig. 7A), which are likely associated with “background” inputs of atmospheric fallout or riverine inputs of combustion-derived PAH. Also prominent in the pre-spill PAHs is perylene (Fig. 7A), which has been long associated with biomass precursors (Venkatesan, 1988). (As noted above, perylene is excluded from the calculation of TPAH50.)

During the oil spill the flux of TPAH50 dramatically increased (Fig. 4B), and averaged $5.4 \pm 5.70 \mu\text{g}/\text{m}^2/\text{day}$ throughout the spill (Table 2). The character of the PAH present in the VK826 trap samples demonstrates the clear presence of petroleum-derived (petrogenic) PAHs (Fig. 7B-H). These PAHs are initially dominated by 3-ring alkylated phenanthrenes with lesser amounts of alkylated fluoranthenes, pyrenes, benz(a)anthracenes, and chrysenes and sulfur-containing alkyl-dibenzothiophenes and naphthobenzothiophenes (Fig. 7B). Two-ring naphthalenes, which are the dominant PAHs present in fresh Macondo oil (Stout 2015b), are markedly reduced in the sediment trap samples. Notably, the retention of decalins (D0-D4) in the face of reduced amounts of the comparably volatile but more soluble naphthalenes suggests that dissolution and/or biodegradation (and not just evaporation) had already affected the “first arriving” oil at the trap (Fig. 7B). Over the course of the spill the character of the PAHs exhibits an overall weathering trend, as was observed in the TPH chromatograms. The PAHs in the trap samples become increasingly dominated by higher molecular weight alkylated chrysenes (Fig. 7B-E) that themselves become increasingly dominated by the C₄-alkylated homologue (Fig. 7E). The shift in PAHs toward higher molecular weight PAHs and more highly alkylated homologues is consistent with the effect of biodegradation (Elmendorf et al., 1994), although dissolution may also contribute.

Coincident with the second “pulse” of oil that arrived at the trap during the oil spill (Fig. 4), and as was the case for the TPH (Fig. 6F), the PAHs also become somewhat “fresher” wherein decalins are again present and alkylated phenanthrenes are again dominant (see D0-D4 in Fig. 7F). Continued weathering of the later arriving oils then, once again, shifts the PAHs toward higher molecular weight PAHs and more highly alkylated homologues (Fig. 7H).

After the well was capped the flux of PAHs quickly dropped to pre-spill levels (Fig. 4, Table 2), and averaged only 0.14 ± 0.12 and $0.28 \pm 0.25 \mu\text{g}/\text{m}^2/\text{day}$ (Post-spill A and B, respectively; Table 2). These post-spill fluxes approximate the TPAH50 flux that had existed prior to the spill ($0.20 \pm 0.16 \mu\text{g}/\text{m}^2/\text{day}$; Table 2). The distribution of PAHs measured in trap samples after the spill were also relatively enriched in Priority Pollutant PAHs (and perylene; Fig. 7I), providing no evidence for lingering oil long after the active spill ceased.



Notably, detailed features among PAH isomers provide evidence that the oil reaching the VK826 trap samples during the active spill originated from oil that was once at the sea surface, rather than from oil derived from any deep sea plume. Specifically, it is well known that photo-oxidation can preferentially affect aromatic compounds in petroleum released into the environment (Garrett et al. 1998; Plata et al. 2008). Isomers of some of the C₁-fluoranthrenes/pyrenes and benzofluorenes are particularly susceptible (CEN, 2012) and, thus, evaluating these compounds' isomer pattern can reveal evidence of photo-oxidation. Figure 8 shows the partial extracted ion profiles for methyl-fluoranthrenes and methyl-pyrenes (*m/z* 216) for fresh Macondo crude oil and for the sediment traps samples at the beginning and end of the spill (i.e., samples "B" and "H", per Figure 4). Inspection reveals that the oils from the trap samples have experienced a preferential loss of 1-methylpyrene and all three benzofluorene isomers relative to 4- and 2-methylpyrene, consistent with photo-oxidation (Fig. 8). This indicates that the oil found in the sediment traps had once been at the sea surface and exposed to *uv* radiation.

Finally, it is worth noting that between April 28 and July 19, 2010 approximately 220,500 to 310,400 barrels (bbls) of floating Macondo crude oil were consumed, reportedly, in 411 separate *in situ* burn events (Mabile and Allen, 2010; Perring et al. 2011). At least some fraction of the uncombusted emissions from these fires might be reasonably expected to have returned to the sea surface and settled through the water column. Priority Pollutant PAHs (i.e. non-alkylated parent PAHs) are known to be abundant in partially combusted organic matter (Blumer and Youngblood 1975). The sediment trap samples collected at VK826 and VK906 have only trace amounts of Priority Pollutant PAHs and thus do not appear to have collected sinking *in situ* burn residues.

Petroleum Biomarkers

As noted above, hopane fluxes showed a dramatic increase in the VK826 trap samples immediately following the start of the *Deepwater Horizon* oil spill, remained high and exhibited a double pulse over the duration of the spill, and a sharp decline after the well was shut-in (Figs. 4C). Hopane, of course, is only one of the targeted biomarkers present in crude oil – but in the case of the sediment trap samples studied, hopane was the most abundant biomarker detected and easily monitored. The distribution, or "fingerprint" of all targeted biomarkers is an important means to distinguish among different petroleum (Wang et al. 2006). In this instance, the distribution of biomarkers is another means to confirm the presence of Macondo oil (versus any "different" oil) within the sediment trap samples.

Figure 9 shows hopane-normalized histograms of all targeted biomarkers – triterpanes, regular and dia-steranes, and triaromatic steroids (TAS) – in the same suite of trap samples shown in Figures 4 to 7. For comparison, also shown in Figure 9 are the average biomarker distributions for fresh Macondo oil (Stout, 2015b) and for floating Macondo oils from 2010 (Stout, 2015c).

Prior to the spill the trap particulates from the VK826 area contain very low concentrations of biomarkers, most being undetectable (Fig. 9A). On average, the flux of hopane was only 0.02 ± 0.01 $\mu\text{g}/\text{m}^2/\text{day}$ prior to the spill (Table 2). The most prominent compounds detected in the pre-spill samples (which plot off-scale in Fig. 9A) are four interfering compounds that happen to co-elute with targeted triterpenoids, (T11a, T20, T26, and T35). These interferences are commonly recognized in marine



sediments and are believed to be derived from biomass (bacterial or plant; Simoneit 1986; Kennicutt and Comet 1992; Hood et al. 2002; Dembicki and Harry 2010). Most of these compounds are unidentified triterpenoids that produce a m/z 191 fragment during mass spectrometry; the interferant present at T20 (which co-elutes with the targeted $17\beta(\text{H})$, $21\alpha(\text{H})$ -moretane) is likely $17\beta(\text{H})$, $21\beta(\text{H})$ -30-norhopane.

Immediately following the start of, and throughout the duration of the *Deepwater Horizon* oil spill, the VK826 sediment trap samples exhibited high fluxes of hopane (Fig. 4C) that averaged $0.89 \pm 0.95 \mu\text{g}/\text{m}^2/\text{day}$ (Table 2) with complete suites of triterpanes, steranes, and TAS being present (Fig. 9B-H). The profiles of these biomarkers closely match those of the fresh Macondo oil (Stout, 2015b) and floating Macondo oils collected in the spring and summer of 2010 for surface waters in the northern Gulf of Mexico (Stout, 2015c; Fig. 9B-H). The distributions of triterpanes and steranes match very well, except for differences due to the aforementioned interfering triterpenoids (light blue bars; Fig. 9). However, all four TAS congeners in the trap samples are present in relatively lower concentrations than in fresh or (on average) floating Macondo oil (see yellow bars; Fig. 9B-H), which we attribute to weathering.

Specifically, the floating Macondo oils had, on average, also experienced a reduction in TAS relative to fresh oil (Fig. 9), with the most severely weathered floating oils containing TAS in comparable abundance as the trap samples (Stout, 2015c). This reduction in TAS was also observed by other researchers who attributed it to photo-oxidation of these photo-reactive (polycyclic aromatic) biomarkers (Aeppli et al. 2014; Radovic et al. 2014), although some dissolution or, perhaps even biodegradation, of these aromatic biomarkers also seems possible. Regardless, this difference in biomarker fingerprints of the trap samples *versus* fresh or floating Macondo oil is readily attributable to weathering, and does not indicate the presence of a “different” oil. Assuming photo-oxidation caused (or, at least, contributed to) the reduction in TAS, this would further indicate that the oil reaching the VK826 sediment trap during the spill had once been at the sea surface and exposed to *uv* radiation (see previous discussion on photo-oxidation of PAH isomers given above; Fig. 8).

After the well was shut-in on July 15, the sediment trap samples exhibited average flux rates of hopane that, given the error, were indistinguishable from those present before the spill (0.03 ± 0.02 versus $0.02 \pm 0.01 \mu\text{g}/\text{m}^2/\text{day}$; Table 2). The triterpanes in these post-spill samples became increasingly dominated by the interfering triterpenoids associated with biomass, although a full suite of regular and diasteranes mostly consistent with Macondo oil were still present (Fig. 9I). In fact, trap samples exhibiting suites of steranes and diasteranes persisted in VK826 trap samples until mid-November 2010, i.e., four months after the well was shut-in, before finally becoming undetectable. Because such suites of steranes and diasteranes were not present in trap samples collected prior to the spill (Fig. 9A), their persistence suggests that some “lingering” vestiges of the Macondo oil may have still been sinking in the VK826 area for up to four months after the end of the active spill.

Volume of Macondo Oil Deposited in Viosca Knoll based on Trap Results

Converting the observed sedimentation rates for Macondo oil-derived hydrocarbons during the active spill (Table 2) into the volume of Macondo oil deposited on the seafloor in the VK826 area is best achieved using the sedimentation rate for hopane, which is considered a conservative marker for the Macondo oil within the trap samples. Specifically, because the concentration of hopane in the fresh liquid Macondo oil is



known (68.8 $\mu\text{g/g}$; Stout, 2015b), and because hopane is not considered to have been lost due to weathering, the mass of liquid Macondo oil represented in the sediment trap samples collected can be calculated from the hopane fluxes for each sampling interval during the spill. In addition, because the density of fresh Macondo oil is also known (0.856 g/cm^3 at 5°C; Stout, 2015d), the calculated *mass* of oil deposited can also be converted to *volume*. The results of these calculations are given in Table 3. The total volume calculated assumes that the oil deposited was fresh Macondo oil (which we know was not the case; see above) and therefore does not include the volume of any expelled oil that was lost to weathering *before* reaching the VK826 sediment traps/seafloor. Nonetheless this calculation provides information on the total oil budget for the *Deepwater Horizon* oil spill.

The average “background” hopane sedimentation rate at the VK826 site (0.02 $\mu\text{g/m}^2/\text{day}$; Table 2) must first be subtracted from the total (“background” plus spill) hopane sedimentation rates for each of the seven samples (B to H; Fig. 4) collected during the active spill (and clearly comprised of Macondo oil; see above). The mass and volume of Macondo oil represented by each sample can then be summed to provide an estimate of the total mass and volume of Macondo oil deposited during the active spill. The results show that, during the active spill a total of approximately 10 barrels (bbls) of Macondo oil per km^2 was delivered to the seafloor at the VK826 area (Table 3).

Implications of VK826 Sediment Trap Results

The VK826 (*Lophelia* reef) location, at a depth of ~ 450m, was too shallow to have been impacted by oil within the deep-sea plume that was restricted to water depths >1000m (Camilli et al., 2010). Therefore, the new VK826 sediment trap results clearly show that some fraction of the Macondo oil from the sea surface (as evidenced by photo-oxidation of the oil; Fig. 8) sank to the seafloor throughout the duration of the *Deepwater Horizon* oil spill. Oil from the deep-sea plume clearly was not the only source of oil to reach the seafloor.

More importantly, the phenomenon of Macondo oil from the sea surface sinking to the seafloor evident at the VK826 site was not unique to this location. Logic dictates that the process of oil sinking to the seafloor after once reaching the surface was widespread and occurred over large regions of the northern Gulf of Mexico.

How widespread was the phenomenon? As described above, a combination of factors likely controlled the flux of oil from the sea surface to the seafloor at any given location. The most critical factor in this process was likely the presence of surface oil above the location, a parameter that was assessed continuously throughout the northern Gulf of Mexico during and after the spill (April 25-July 28, 2010) using a variety of satellite sensors (Graettinger et al. 2015).

Figure 10 shows the cumulative oil days for the region from April to mid-August 2010 reported by Graettinger et al. (2015). The VK826 (and VK906) sediment trap(s) occur within an approximately 7600 km^2 “footprint” indicated to have experienced more than 30 days of oil present at the surface, which we have indicated by the dashed line (Fig. 10). As can be seen, some areas inside of this 7600 km^2 area, including the VK906 site, experienced more (above 40 or even 50) oil days while areas outside of this 7600 km^2 area experienced fewer (but more than zero) oil days.

It is reasonable to assume that flux of surface oil to the seafloor occurred over the entire region, but were likely higher in areas that experienced more oil days and *vice versa*. At a minimum, we can conservatively assume that surface oil sank to the seafloor within the 7600 km^2 footprint that encompasses the VK826 (and VK906) site(s) at a rate



represented by the VK826 settling-rate fluxes reported here. Notably, approximately half of this 7600 km² area occurs in water depths less than 1000 m and even extends onto portions of the shelf (<200 m; Fig. 10).

Even considering the 7600 km² area as conservative, it is much larger than the area of seafloor previously-recognized to have been impacted by sunken Macondo oil. For example, based upon Kriging of non-background/non-seep hopane concentration in surface sediments (as established through chemical fingerprinting; Stout 2015a), Stout et al. (2015) recognized between 1030 and 1910 km² of deep seafloor had been measurably impacted by Macondo oil (see Fig. 10). The 7600 km² area conservatively considered, here, to have been impacted by marine oil snow formed at/near the surface (i.e. from MOSSFA) is 5- to 7-times larger than the seafloor “footprint(s)” previously-recognized through sediment chemistry to have been impacted by fall-out from the deep-sea plume.

It is fair to ask, *why didn't existing sediment studies (e.g., Valentine et al., 2014; Stout et al., 2015) recognize a larger benthic “footprint”?* We believe the answer to this question is two-fold. First, existing sediment studies were constrained by the available sediment core data. Most of the 728 sediment cores were collected from the deep sea (>1000 m) with only a few collected on the slope or shelf (Fig. 1). The low sample density of sediment cores collected from these shallower areas provided low spatial resolution that precluded the ability to statistically recognize any impact in areas of low sampling density, although some impact was suspected (Valentine et al., 2014). Second, the fluxes reported here for VK826 were transient and would not be so readily detectable from the time-integrated sampling that sediment coring represents. Consequently, the effects of dilution on the concentration of any Macondo oil deposited at the surface of cores, which were sampled with resolutions of 0-1 cm to 0-2 cm, undoubtedly impeded the ability to recognize excess hopane or to chemically fingerprint the hydrocarbons present in areas where only Macondo oil had sunk (i.e., outside the “footprints” recognized by Stout et al., 2015; Fig. 10).

Specifically, the predicted concentrations of Macondo-derived TPAH50 and hopane in the surface (0-1 cm) sediment layer can be made using the average sedimentation rates for each obtained from the VK826 trap data (Attachment 3). These calculations show the predicted concentrations of Macondo-derived TPAH50 and hopane deposited as marine snow in the VK826 area during the active spill in the upper 0-1 cm of sediment are $19.8 \pm 21.7 \mu\text{g/g}$ and $3.3 \pm 3.6 \mu\text{g/g}$, respectively. Although these low concentrations are above the typical analytical reporting limits for sediments, in practice their impact may be difficult to recognize, let alone attribute to Macondo oil. In addition, the deposition of marine oil snow particles was likely heterogeneous (e.g., many particles in one small area and few in an adjacent area), meaning that some sediment cores (typically on ~2.5 inches diameter) might encounter higher or lower concentrations of particles containing Macondo oil.

Despite these practical considerations, some of the six sediment cores collected in October 2011 from the VK826 and VK906 sites do show increases (albeit slight) in the concentrations of TPAH50 and/or hopane in the surface layers, while other cores show quite consistent concentrations of TPAH and hopane throughout (Fig. 11). The increased concentration at the top of some cores and lack of increases in others likely speaks to the heterogeneities consistent with particle (marine oil snow) deposition. Those cores exhibiting increases, however, when viewed in light of the VK826 sediment trap data presented here, suggests that Macondo oil-derived PAH and hopane did contribute to the total hydrocarbons in the surface sediments. (It is also notable that



these particular sediment cores were collected more than a year after the Macondo marine oil snow was deposited during the active spill. Over this time multiple chemical, biological, or physical processes may have reduced the Macondo-derived hydrocarbon concentrations measured in surface sediments.) By extension, sediments in other shallow (< 1000 m) areas that experienced frequent oil days are also likely to have been similarly impacted by Macondo-derived hydrocarbons associated with marine oil snow.

How much oil was deposited on the seafloor through marine oil snow formed at/near the surface? If it is assumed, conservatively, that the volume of oil deposited near the VK826 site (10 bbl/km²; Table 3) is representative of the whole 7600 km² of the 30+ oil days area, it can be roughly estimated that approximately 76,000 bbl of oil that had once been part of the surface oil-slick may have sunk within the 7600 km² footprint indicated (Fig. 10). Of course, what is more likely is that the volume of surface-slick oil that sank closer to the wellhead, in the area that experienced more oil days (>40 or >50; Fig. 10) was even higher. In addition, some additional volume of surface oil likely sank outside the 7600 km² area (i.e., in the area that < 30 oil days; Fig. 10). Therefore, although only roughly estimated, we consider the 76,000 bbl of surface oil predicted here to have sunk to the northern Gulf of Mexico seafloor after reaching the surface estimate to be a minimum volume.

How does this volume compare to the volume of oil on the seafloor derived from the deep-sea plume? Using the same hopane-based method to estimate oil volume employed herein, Stout et al. (2015) estimated a total of 152,000 bbl and 173,000 bbl of Macondo oil was present on the seafloor surface (0-1 cm) within their minimal (1,030 km²) and maximal (1,910 km²) deep-sea “footprints”, respectively.¹ Because these deep-sea, surface sediment “footprints” mostly fall within the 7600 km² area over which 76,000 bbl of surface oil had sunk (Fig. 10), some portion of the total Macondo oil (i.e., 10 bbl/km²) within each of these deep-sea surface sediment “footprints” was derived from sunken surface oil.

Calculations show that 7 to 11 percent (by volume) of the total Macondo oil found *inside* the previously-recognized (minimal and maximal) deep-sea, surface sediment “footprints” was derived from sunken surface oil (Table 4). Oppositely, of course, that means that approximately 93 to 89 percent of the Macondo oil found within these deep-sea, surface sediment “footprints” was derived from deep-sea plume oil (Table 4). We consider these ranges to be representative over the whole of these deep-sea “footprints” but expect lower percentages of sunken surface oil exist closer to the well and *vice versa*. Regardless, overall within the deep-sea, surface sediment “footprints” the dominant source of oil reaching the seafloor was the deep-sea plume (89 to 93%) – as was concluded based upon the geometry of the previously-recognized deep-sea “footprints” (Valentine et al., 2014; Stout et al., 2015).

Additional calculations reveal that 65,700 to 56,900 bbl of sunken surface oil was deposited on the seafloor *outside* of the previously-recognized deep-sea “footprints” but within the 7600 km² area (Table 4). These additional and substantial volumes of sunken surface oil were unrecognized prior to this work. As noted above, we believe these are minimum volumes. These added volumes of previously-unrecognized sunken surface

¹ Stout et al. (2015) also determined approximately 67,000 to 74,000 bbl of Macondo oil was deposited in subsurface (> 1 cm) sediments near the well. These volumes are envisioned to have been overwhelming deposited by direct fallout from the well, and not from marine oil snow. As such they are excluded from the discussion here, which is focused on marine oil snow contributions to surface sediments outside the immediate fallout zone around the well. These additional volumes, nonetheless, should be included in any total “sunken” oil estimates.



oil represent a 33 to 43 percent increase in the total volume of Macondo oil previously-recognized to have been deposited on the seafloor surface based on sediment chemistry of cores (Table 4).

In total, the combined sediment core-based results that focused in the deep-sea, surface sediments (>1000m; Stout et al., 2015) and our sediment trap-based results from the shallower region of the northern GoM (< 1000m; this work), indicate a total of at least 217,700 to 229,900 bbl of oil ended up on at least 7600 km² of seafloor surface following the *Deepwater Horizon* oil spill (Table 4).¹

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Table 1: Inventory of sediment trap samples studied. Locations shown in Figure 1. Complete listing of samples from each trap is provided in Attachment 1.

	Trap ID	Distance to Macondo (km)	Lat (N)	Long (W)	Sea-floor (m)	Trap Depth (m)	Start Date	End Date	Interval (days)	Samples available for study
VK826 Site										
NOAA/BOEM	GOMEX M2 VK01	58	29°09.55'	88°01.13'	463	457	11-Sep-09	2-Jul-10	14	21
NSF	RR1 M2 VK02		29° 09.62'	88°01.13'	452	426	25-Jun-10	7-Jan-11	15	13
NRDA	RR3		29°09.61'	88°01.12'	450	424	16-Mar-11	14-Sep-11	14	13
										47
VK906 Site										
NRDA	RR2 M1	37	29°04.17'	88°22.64'	427	401	29-Jul-10	27-Oct-10	6	6
NRDA	RR2 M2		29°06.44'	88°23.09'	332	306	29-Jul-10	15-Oct-10	6	13
*incomplete suite; missing some intervals										19
MC751										
NOAA/BOEM	GOMEX M1 MC01	153	28°11.64'	89°47.90'	436	430	11-Sep-09	20-Nov-09	14	5



Table 2: Sedimentation rates (mean and standard deviation; $\mu\text{g}/\text{m}^2/\text{day}$) of TPH, TPAH50, and hopane in sediment trap particulates from Viosca Knoll (VK826) collected before, during and/or after the *Deepwater Horizon* oil spill. Calculated from data in Attachment 1.

	n	TPH		TPAH50		Hopane	
		mean	σ	mean	σ	mean	σ
VK826 Site							
Pre-Spill	16	124	144	0.20	0.16	0.02	0.01
Spill	7	2356	1919	5.4	5.7	0.89	0.95
Post-Spill A ¹	11	108	53	0.14	0.12	0.03	0.02
Post-Spill B ²	13	142	116	0.28	0.25	0.03	0.02
¹ late July 2010 to early Jan. 2011							
² mid-March to mid-Sept. 2011							



Table 3: Hopane-based sedimentation rate for Macondo oil for the seven trap samples collected during the active spill showing the total volume (bbl/km²) of Macondo oil deposited in the VK826 area during the *Deepwater Horizon* oil spill. Total is corrected for “background” oil as represented by the average for 16 pre-spill samples (from Table 3). Note nearly half of the total oil (4.6 of 9.5 bbl/km²) was deposited during the 15-day period (June 25-July 10, 2010), i.e., the second “pulse” of oil (see text; RR1 M2 VK02-01).

Sample	Figure Label	Total Hopane Flux (ug/m ² /day)	"Pre-Spill" Hopane Flux (ug/m ² /day) (Avg; n=16)	Macondo Hopane Flux (ug/m ² /day)	Macondo Oil Flux-Mass (kg/km ² /day)	Macondo Oil Flux-Volume (bbl/km ² /day)	Macondo Oil Volume (bbl/km ² per deployment period)
GOMEX M2 VK01-17	B	0.18	0.02	0.16	2.35	0.02	0.2
GOMEX M2 VK01-18	C	0.62	0.02	0.60	8.68	0.06	0.9
GOMEX M2 VK01-19	D	0.19	0.02	0.17	2.45	0.02	0.3
GOMEX M2 VK01-20	E	0.32	0.02	0.30	4.41	0.03	0.5
GOMEX M2 VK01-21	F	1.00	0.02	0.98	14.20	0.10	1.5
RR1 M2 VK02-01	G	2.90	0.02	2.88	41.88	0.31	4.6
RR1 M2 VK02-02	H	1.02	0.02	1.00	14.57	0.11	1.6
¹ Fresh Macondo contains 68.8 mg/kg hopane							
² Fresh Macondo density at 5°C 0.856 g/ml; 42 gal = 1 bbl							
Cumulative Total of Macondo Oil Deposited at VK826 During Spill:							10
							bbl/km ²



Table 4: Calculations of the volumes (percentages) of Macondo oil found on the seafloor based upon results of a previous study of deep-sea sediments (Stout et al., 2015) and the new VK826 sediment trap results. See text for description.

	Previously-Recognized Deep-Sea "Footprint" ¹	
	Minimal	Maximal
Deep-Sea Surface Sediment Footprint		
Area (km ²) ¹	1030	1910
Volume oil - Total on seafloor within deep-sea "footprint" (bbl) ¹	152,000	173,000
Volume oil - Sunken surface oil contribution to the deep-sea "footprint" (bbl) ²	10,300 (7%)	19,100 (11%)
Volume oil - Sunken deep-sea plume oil within deep-sea "footprint" (bbl) ³	141,700 (93%)	153,900 (89%)
Sunken Surface Oil Footprint		
Area (km ²) ⁴	7600	7600
Volume oil - Total sunken surface oil within sunken surface oil "footprint" (bbl) ²	76,000	76,000
Volume oil - Sunken surface oil contribution to the deep-sea "footprint" (bbl) ²	10,300	19,100
Volume oil - Sunken surface oil deposited outside deep-sea "footprint" (bbl) ³	65,700	56,900
Summary		
Volume oil - Total on seafloor within deep-sea "footprint" (bbl) ¹	152,000 (70%)	173,000 (76%)
Volume oil - Total sunken surface oil outside deep-sea "footprint" (bbl) ²	65,700 (30%)	56,900 (24%)
Volume oil - Total oil reaching the seafloor within 7600 km ² area (bbl) ⁴	217,700	229,900
Percent Increase in total oil reaching the seafloor due to sinking surface oil	43	33
¹ Stout et al. (2015); excludes seep oil and subsurface (> 1 cm) Macondo oil nearest the well		
² assume 10 bbl/km ² per VK826 trap results		
³ by difference		
⁴ 30+ oil days (Fig. 10)		

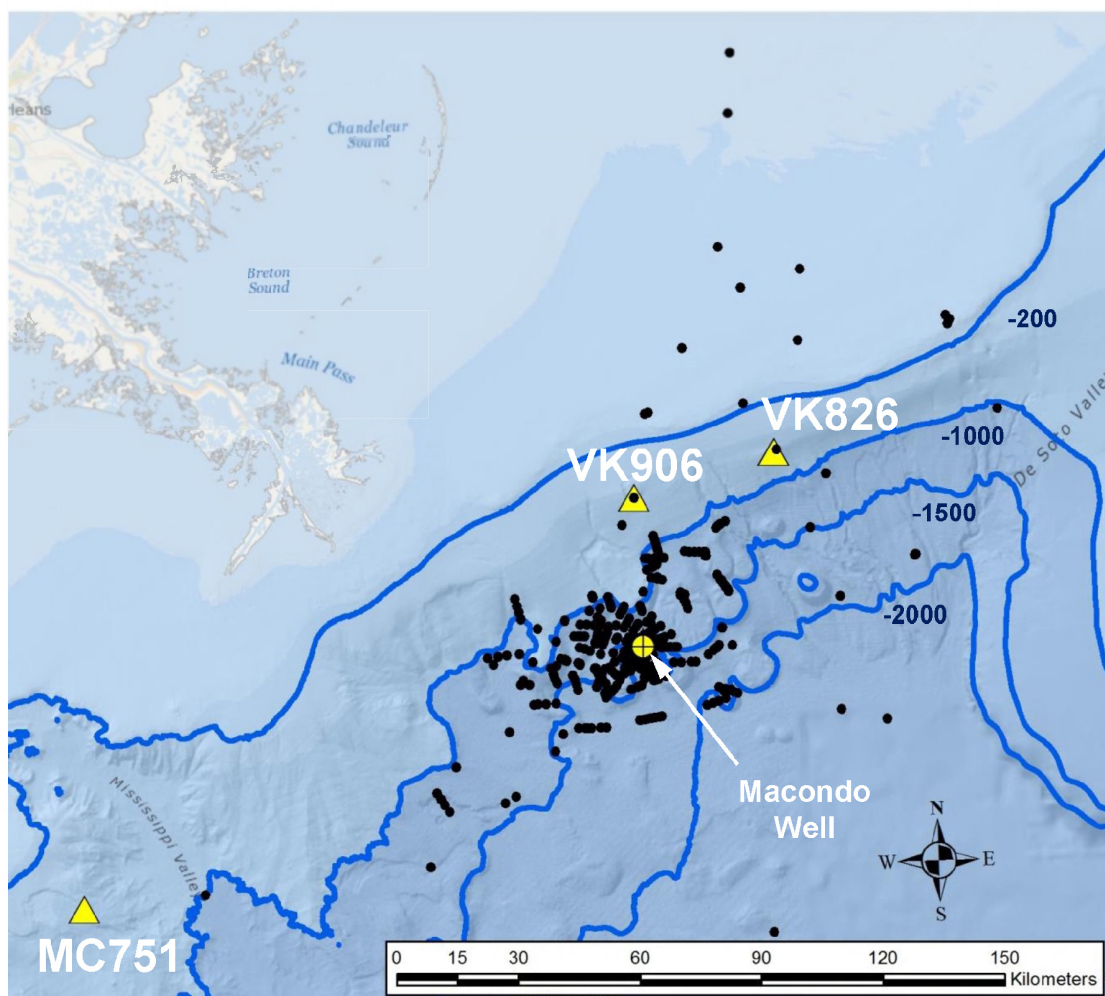


Figure 1: Map showing the location of the Viosca Knoll (VK906 and VK826) and Mississippi Canyon (MC751) sediment traps (yellow triangles). Bathymetric contours (m) and locations of 728 sediment cores collected as part of the NRDA investigation (black dots) are indicated. Note only a limited number of sediment cores were collected at depths less than 1000 m with only a few located at the Viosca Knoll sediment trap sites.

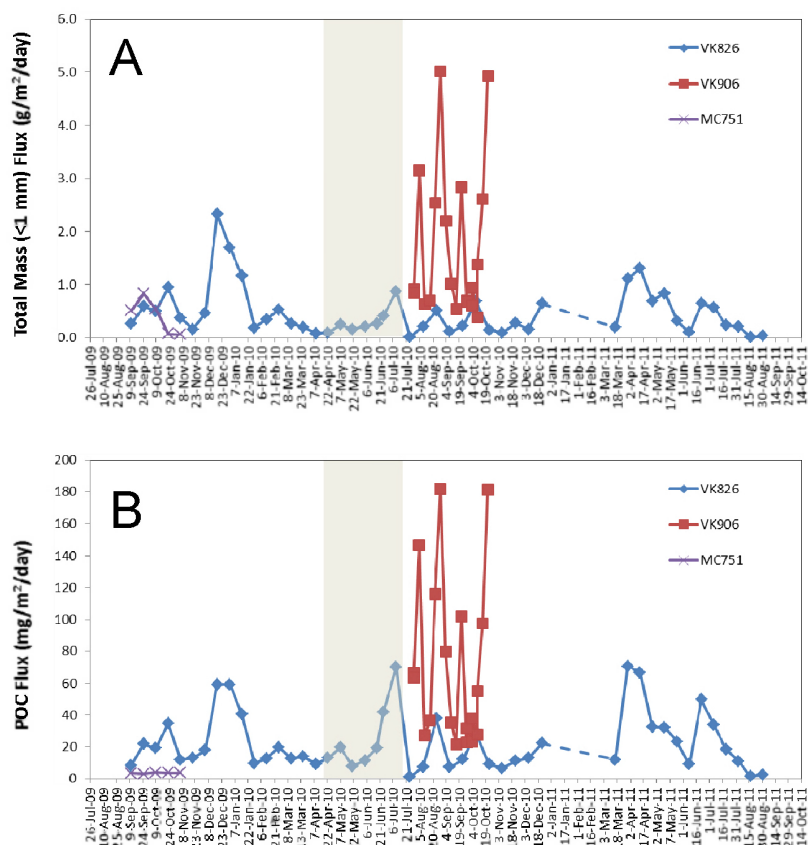


Figure 2: Plots showing the temporal trends in sedimentation rates of (A) total mass of particulate (< 1 mm) and (B) particulate organic carbon (POC) in the sediment trap samples studied. Trap "open date" plotted on x-axis. All data from Attachment 1. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010). No clear association exists between the sedimentation rates of total particulate mass or POC and the oil spill.

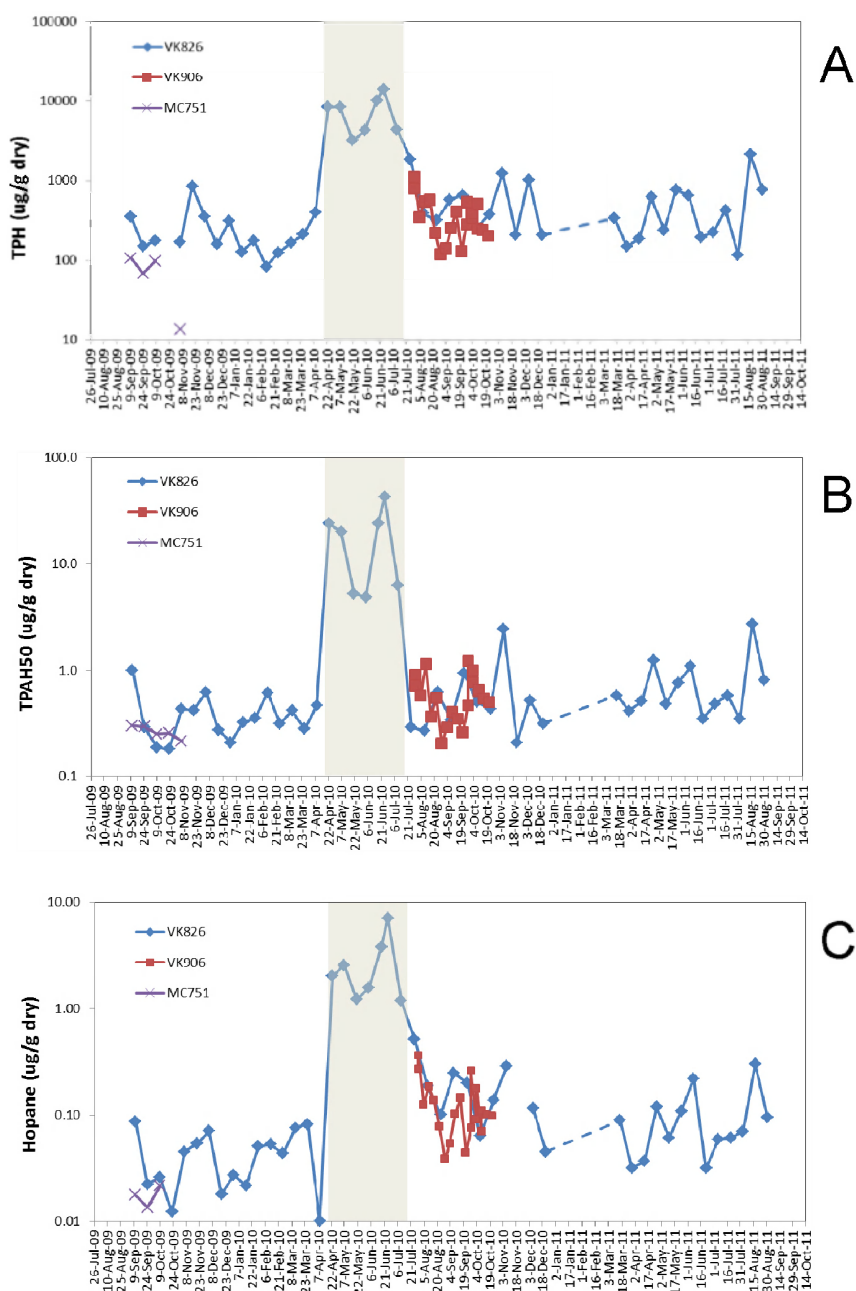


Figure 3: Plots showing the temporal trends in the concentrations of (A) TPH, (B) TPAH50, and (C) hopane in particulates (< 1 mm) in the sediment trap samples studied. Trap “open date” plotted on x-axis. All data from Attachment 1. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010). Note log-scale on each.

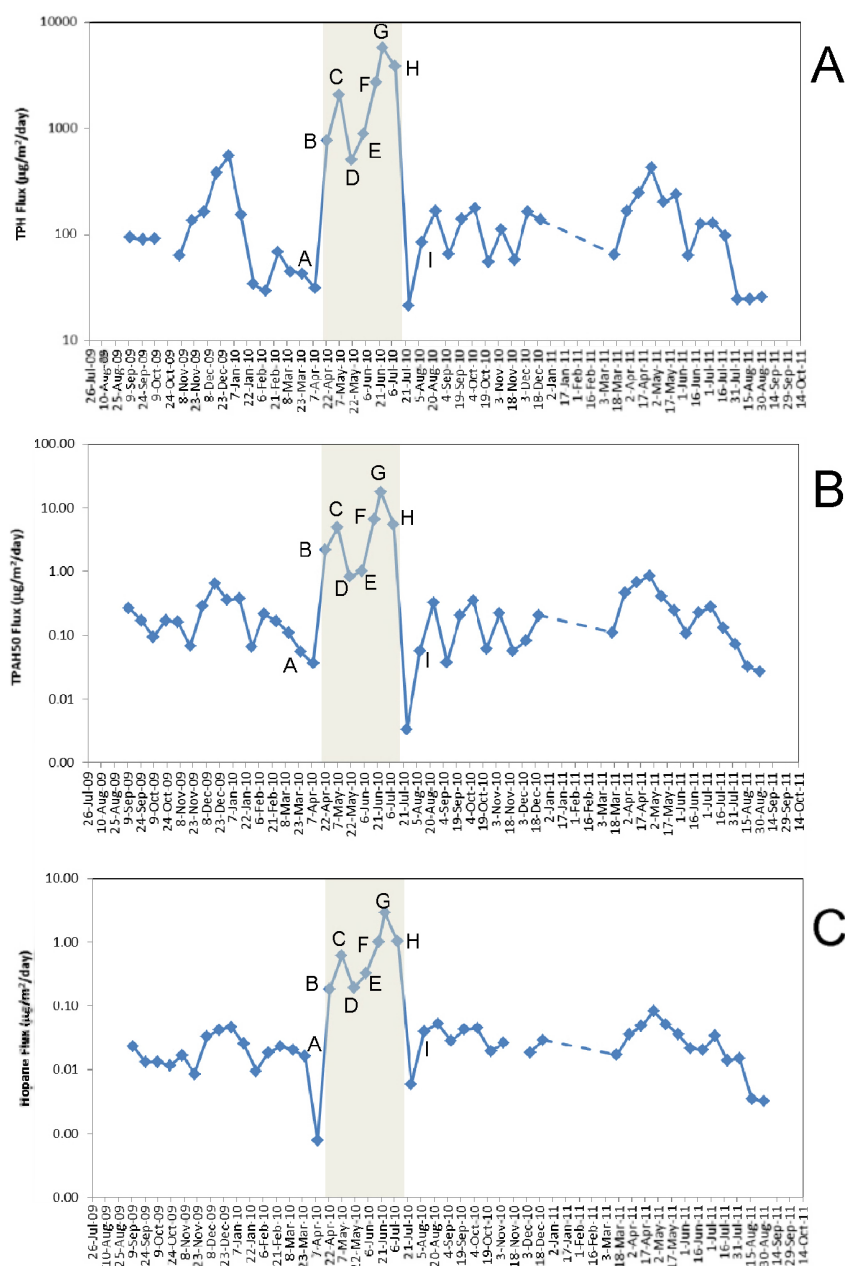


Figure 4: Plots showing sedimentation rates for (A) TPH, (B) TPAH50, and (C) hopane in Viosca Knoll 826 sediment trap samples studied. Trap “open date” plotted on x-axis. All data from Attachment 1. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010). Note log-scale on each. Small letters (A through H) refer to individual sample data shown in Figs. 5, 6, 7 and 9.

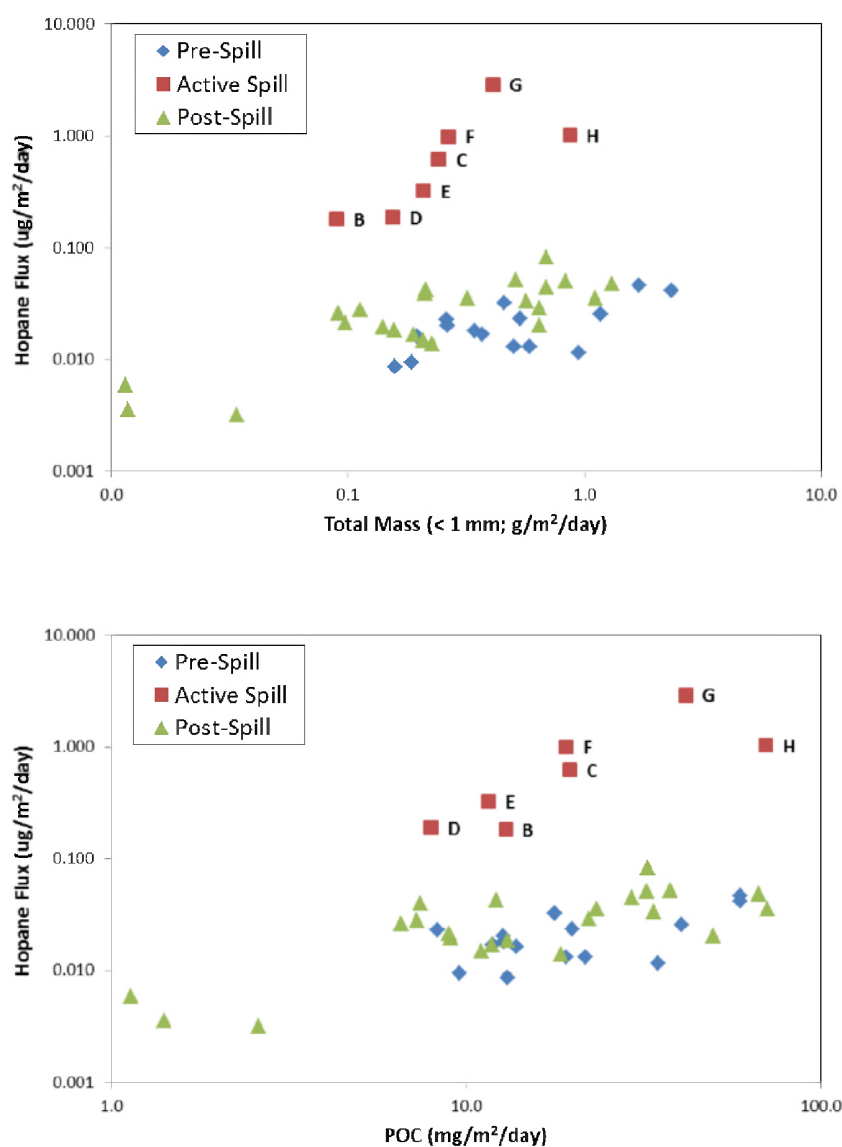


Figure 5: Plots showing relationships between the sedimentation rates for hopane and (A) total mass of particulate $<1 \text{ mm}$ and (B) POC in VK826 the sediment trap samples studied. All data from Attachment 1. Active spill sample labels correspond to those shown in Figure 4. Note log-scale on each.

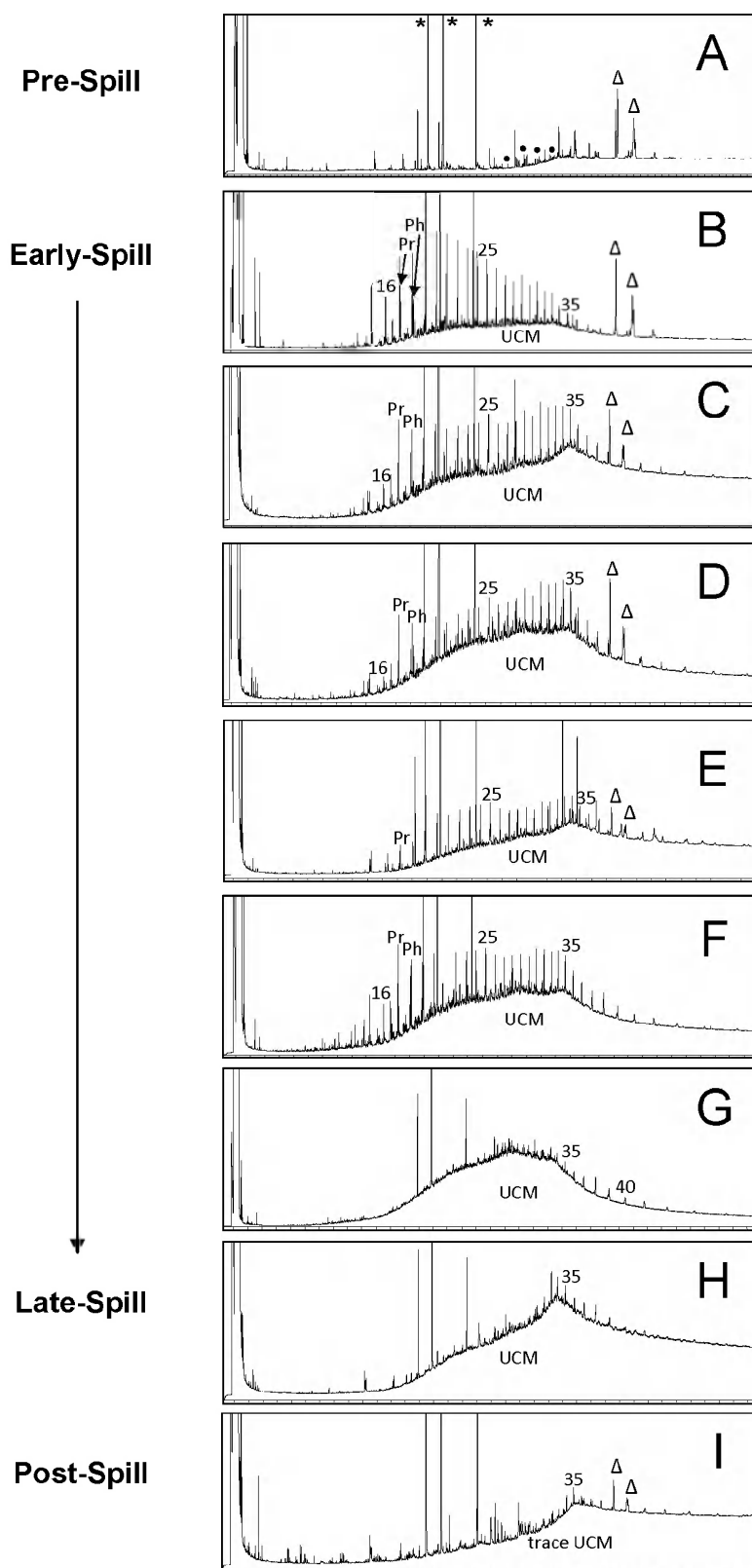


Figure 6: GC/FID chromatograms for TPH in sediment trap samples from VK826 site. (A) pre-spill (March 26, 2010), (B) through (H) represent the samples collected during the active spill, and (I) post-spill (Aug. 9, 2010). Refer to Figure 4 for labels (A) through (I).

* - internal standards; Δ - unknown marine snow constituents attributed to biomass (not oil); # - n-alkane carbon number; Pr-pristane; Ph-phytane; • - odd n-alkanes (27-33); UCM – unresolved complex mixture.

Label	Sample/Open Date
A	GOMEX M2 VK01-15 3/26/2010
B	GOMEX M2 VK01-17 4/23/2010
C	GOMEX M2 VK01-18 5/7/2010
D	GOMEX M2 VK01-19 5/21/2010
E	GOMEX M2 VK01-20 6/4/2010
F	GOMEX M2 VK01-21 6/18/2010
G	RR1 M2 VK02-01 6/25/2010
H	RR1 M2 VK02-02 7/10/2010
I	RR1 M2 VK02-04 8/9/2010

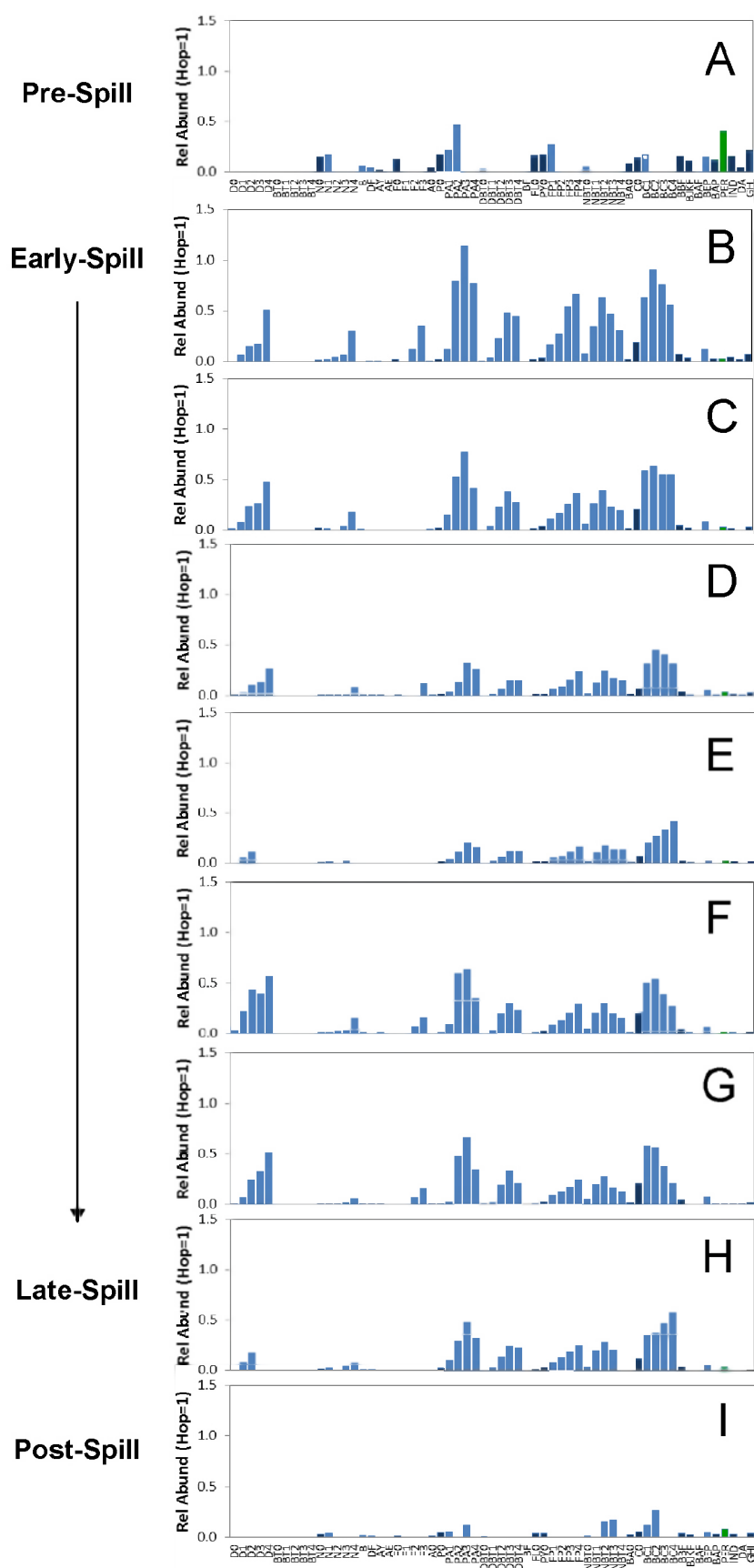


Figure 7: Hopane-normalized histograms showing relative concentrations and distributions of PAH in sediment trap samples from VK826 site. (A) pre-spill (March 26, 2010), (B) through (H) represent the samples collected during the active spill, and (I) post-spill (Aug. 9, 2010). Refer to Figure 4 for labels (A) through (I); Caption to Figure 6 contains sample identifications.

See attached data tables for compound abbreviations.

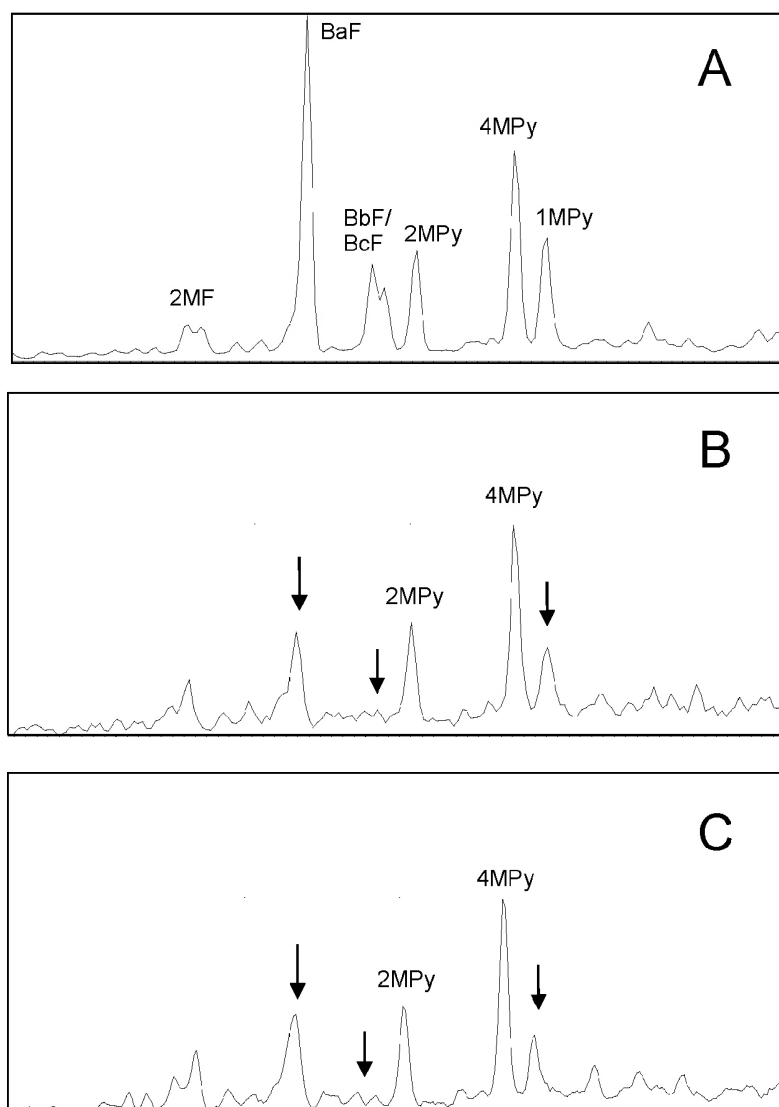


Figure 8: Partial EIPs showing methyl-fluoranthrenes/pyrenes (m/z 216) isomer patterns in (A) fresh Macondo crude oil, (B) “first arriving” oil from VK826 sediment trap (Sample “B” in Fig. 4; GOMEX M2 VK01-17) and (C) later arriving oil from VK826 sediment trap (Sample “H” in Fig. 4; M2 VK02). Isomer specific reductions (arrows) are attributed to photo-oxidation indicating the oil reaching the sediment trap was once at the sea surface.

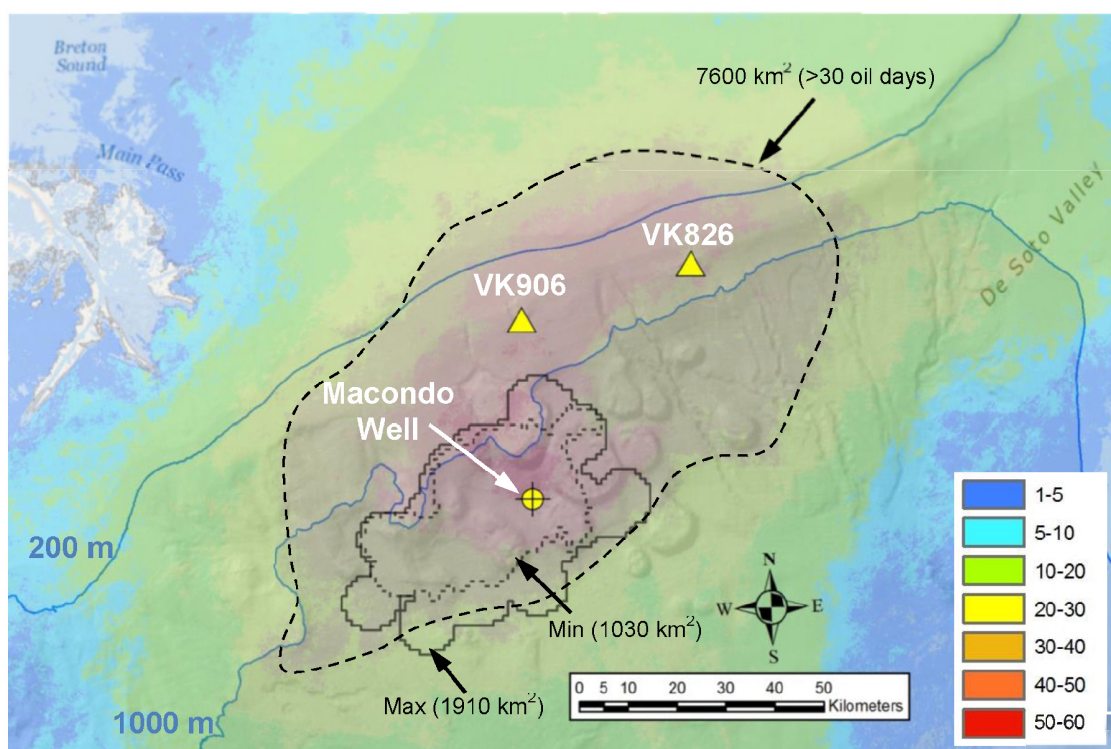


Figure 10: Map showing cumulative oil days (April 25 to July 28, 2010) determine (from Graettinger et al., 2015) relative to the Viosca Knoll sediment traps, Macondo well, and 200 and 1000 m bathymetry contours. Key refers to “oil days”, i.e., total number of days when surface oil was determined to be present using multiple remote sensing methods (Graettinger et al., 2015). The ~7600 km² area which experienced > 30 oil days is indicated (dashed line) along with previously-recognized deep-sea “footprints” (min. and max.) of seafloor sediments containing Macondo oil based upon chemical results of more than 700 sediment cores (Stout et al., 2015). The sediment trap results indicated 10 bbl/km² of surface oil that sunk near the VK826 site indicating, by extension, at least 76,000 bbl of surface oil likely sunk within the entire 7600 km² area that had experienced > 30 days of surface oil. See additional discussion in text.

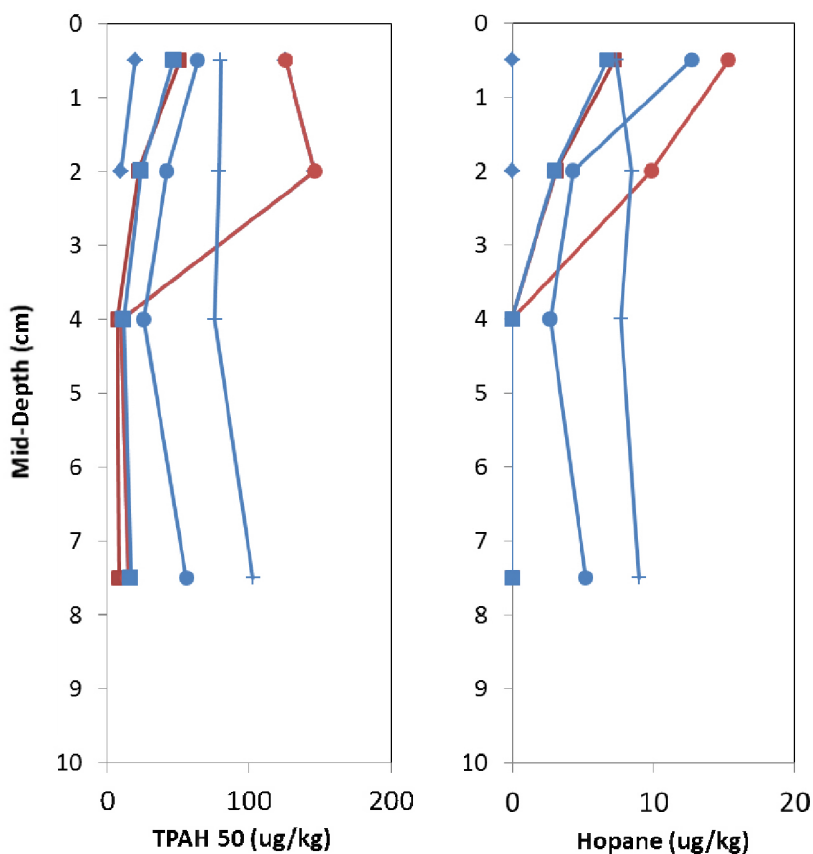


Figure 11: Plots showing the concentration profiles of TPAH50 and hopane in sediment cores collected from the VK826 (red; n=2) and VK906 sites (blue; n=4). Profiles show either an increase in concentration at the uppermost layer(s) or no change throughout the cores. All six cores collected on Holiday Chouest 3 NRDA cruise (Oct. 1-25, 2011). Non-detected concentrations of hopane are plotted as zeros. VK826 cores: HC3-B1022-S-E8-VK826026-HC-016-019 and HC3-B1022-S-E8-VK826026-HC-020-023. VK906 cores: HC3-B1023-S-E8-VK906029-HC-016-017, HC3-B1023-S-E8-VK906029-HC-020-023, HC3-B1023-S-E8-VK906029-HC-051-054, and HC3-B1023-S-E8-VK906029-HC-055-058. Data provided in Attachment 4.